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Observations on the Rare Earths

**OBSERVATIONS ON THE RARE EARTHS.
PURIFICATION OF YTTRIUM AND
SEPARATION OF ERBIUM
AND HOLMIUM**

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

ROGER GREENLEAF STEVENS

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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science

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I. INTRODUCTION

Formerly, the minerals in which the rare earths occur were found in very few places namely, Sweden, Norway and the Ural Mountains. When incandescent gas lighting was introduced, a search for rare earth minerals resulted in the discovery of large tracts of monazite sand and other minerals widely distributed over the surface of the earth, chiefly in Virginia, the Carolinas, California, Brazil, India, and Australia.¹ The rare earths cannot be separated by the usual methods for the separation of metals. The reason for this is found in the fact that the rare earths are so similar in properties, that they display like characteristics when treated with reagents employed in ordinary separations. It is therefore necessary in separating them to depend upon two properties, their basicity, and the varying solubility of their salts in solvents.

The object of this work was to study the two principal methods of the separation of the rare earths, namely, fractional precipitation and fractional crystallization and to prepare pure yttrium and erbium material for further investigation.

The yttrium material was obtained from two sources, Chromates prepared by Dr. B. S. Hopkins² and bromates prepared by Dr. E. W. Engle.³ The material was composed mainly of yttrium with small amounts of erbium and holmium and probably no other rare earths.

1. Chem. Ind., 29 320-32, 350-61, (1906) 38hn.

2. J. A. C. S. 38 2532, (1916)

3. Ibid. 39 53, (1917)

The erbium material of the Bn series was obtained from the combined soluble fractions of a bromate series described in a previous work.¹ It contained mostly erbium with small amounts of holmium and also cerium and neodymium due to incomplete removal of the cerium earths. The material of the Bb series was composed of the more insoluble fractions of the same bromate series. It contained erbium, holmium, and yttrium with small amounts of cerium and neodymium.

1. Ibid, 39 53, (1917)

II. HISTORY OF YTTRIUM AND ERBIUM

Yttrium was discovered by Gadolin¹ in 1794. The mineral was found to contain 38 percent of the oxide which resembled the properties of the oxides of calcium and aluminium. The discovery was later confirmed by Ekeberg² in 1797 who assigned the name yttria to the new oxide. Confirmation was also provided in 1801 by Klaproth and Vauquelin who gave an account of the properties of yttrium. Yttrium occurs in practically all the rare earth minerals but more especially in, gadolinite, xenotime, euxenite, polycrase, and monazite.

In 1843, Mosander³ showed yttrium to be a complex substance being made up of three earths, a colorless substance for which the name yttrium was retained, a rose colored earth, erbium and a yellow earth, terbium. Marignac⁴ in 1878 was able to separate erbia into two oxides of different basicity, one colored red, for which the name erbia was retained and the other, colorless, which was named ytterbium. Cleve⁵ resolved the residue, after the removal of ytterbium, into three earths, erbium, holmium, and thulium. Soret⁶ was able to show upon examination of the salts of these earths that the unknown element which he had discovered in 1878 in crude erbium earths was identical with holmium.

1. Crell's Ann., 1, 313, (1796)
2. Ibid. 2 65, (1799)
3. J. pr. Chem., 30, 276, (1843)
4. Compt. rend., 87 578, (1878)
5. Ibid., 89 478, 708, (1879)
6. Ibid., 89 521, (1879)

Erbium is found in practically all of the rare earth minerals the more important being xenotime, fergusonite, euxenite, polycrase, and blomstrandin.

III. PURIFICATION OF YTTRIUM BY FRACTIONAL PRECIPITATION WITH SODIUM NITRITE

The atomic weight of yttrium has been determined by a large number of investigators and many different results have been obtained. The results prior to a decade ago are of little value as the material which was used for the work was not of the highest purity. The chromate method was shown by Dr. B. S. Hopkins to be unsuitable for the removal of the last traces of either holmium or erbium. However, very good results were obtained with the sodium nitrite method which gave pure yttrium. The atomic weight of the yttrium which was determined at that time has since been accepted by the Committee on International Atomic Weights.

In the present work, the purification of yttrium by the sodium nitrite method was undertaken to study the method of precipitation and also to introduce certain refinements wherever possible. The method as suggested by Holden and James¹ consists in adding a strong solution of sodium nitrite to the nearly neutral solution of the rare earth nitrates.

1. J. A. C. S. 36 1419 (1914)

The nitrates were prepared by igniting the oxalates in a platinum crucible and dissolving the rare earth oxides in pure nitric acid and evaporating to dryness, care being taken to heat gently and not to over heat any portion. In igniting to the oxide, it was found best to fill the crucible about three-quarters full and to have the greatest thickness of the material around the edges with a depression in the center. In this way, the danger of spattering was eliminated which would be caused by the accumulation of carbon dioxide gas and its sudden liberation from time to time. The residue containing the rare earth nitrates was dissolved in water, made up to about 5 liters and heated to boiling over a steam bath. The 8 liter flask was placed on a cork ring in an evaporating dish of sufficient capacity to hold the contents of the flask in case of breakage. Boiling was continued by passing in a lively stream of steam. A strong solution of sodium nitrite was added drop by drop from a separatory funnel. After some time a precipitate formed which increased in volume. The slowness of the formation of the precipitate is probably due to supersaturation, equilibrium being reached with difficulty.

The steam was passed in the solution through two glass tubes, one tube being found inadequate to produce steady and uniform boiling. The tubes were turned up for about an inch at the ends and extended to the bottom of the flask. They were connected to the same source of steam supply by means of a forked tube. A Woulff bottle was placed between the steam supply and the flask, which was for the purpose of holding the condensate which collected in the line, thereby preventing the condensed steam from passing

over into the solution. The boiling was continued for 30-90 minutes after the addition of the nitrite, then the solution was allowed to stand usually over-night. The precipitate was filtered off and washed once or twice with distilled water. The filtrate was evaporated to its former volume of 5 liters and the boiling and precipitation with sodium nitrite repeated until all of the rare earths were removed from the solution. The nitrite used was of the C. P. grade whose purity was proven by the U.S.P. test. The usual amount added at a time was 75 grams dissolved in 150 c.c. water.

The first fractions obtained were small probably due to part of the nitrite being used up by reaction with the nitric acid which was not originally removed during evaporation. The first precipitates were crystalline in structure but, as more and more of the rare earths were removed from the solution, the precipitates became
/gelatinous. The structure of the last precipitates is probably due to the formation of basic nitrites.

The fractions were purified to remove the sodium salts. The precipitate was dissolved in nitric acid and the solution diluted to about 1 liter, heated to boiling and a hot concentrated solution of oxalic acid was slowly added while the flask was being shaken. The heating was continued for 15 minutes and after several hours standing, the precipitate was filtered, washed and dried at 110 degrees C. It was then ignited to the oxide in a platinum crucible. The oxide was dissolved in a small amount of nitric acid, the solution was diluted to 1 liter, heated to boiling and an

excess of ammonium hydroxide was added to the hot solution. The precipitate was filtered, washed and the solution diluted to about 1 liter. The oxalate was precipitated by heating the solution to boiling and as before adding a concentrated solution of oxalic acid until precipitation was complete. This procedure was repeated three times and the oxalate after the final purification was shown by flame analysis to be free from sodium salts.

The oxalic acid was purified by first dissolving it in water, filtering and allowing it to crystallize. The crystals were separated from the mother liquor and dissolved in water containing about 5 c.c. nitric acid per 500 c.c. water. The solution was evaporated until crystals formed. The crystals were filtered off and dissolved again in water containing a small amount of nitric acid. This process was repeated three times and the last crystallization took place in pure water. The oxalic acid as purified left no weighable residue upon ignition. The nitric and sulphuric acids were of the C. P. grade. The water used was distilled from the laboratory still.

IV. DETERMINATION OF THE ATOMIC WEIGHT OF YTTRIUM.

The determination of the atomic weight of yttrium was carried out according to the method of Gibbs.¹ The finely crystalline oxalates after purification, were washed to remove any oxalic acid and dried for several hours at 105-115 degrees C. Each fraction was thoroughly mixed and two samples weighed out. The one sample which weighed about 0.2 grams was ignited to the oxide in a porcelain crucible which had been previously weighed together with the cover. The cover was removed during ignition, but was immediately replaced after ignition as the oxide rapidly absorbs moisture from the air. The crucible was heated to constant weight which was usually obtained after only one heating of about an hour, the oxalate being thoroughly disintegrated with a platinum wire during the course of heating.

The other sample, weighing about 0.1 grams, was dissolved in 25 c.c., 5 normal sulphuric acid, diluted to 250 c.c, heated to boiling and titrated with standard potassium permanganate solution, approximately 0.05 normal. The atomic weight was calculated from the formula: $R = \frac{108 \times \%R_2O_3}{\%C_2O_3} - 24$, where R represents the atomic weight of yttrium in this case.

The formula is derived in the following manner. The percentage of oxide in the sample is represented by the equation:

$$\%Y_2O_3 = \frac{Y_2O_3}{Y_2(C_2O_4)_3} \times 100.$$

1. J.A.C.S. 15, 546 (1893)

The percentage of C_2O_3 , that is, yttrium oxide minus yttrium oxalate or $[Y_2(C_2O_4)_3 - Y_2O_3 = 3C_2O_3]$, is represented by the equation: $\% C_2O_3 = \frac{3C_2O_3}{Y_2(C_2O_4)_3} \times 100$

Therefore:

$$Y_2O_3 : 3C_2O_3 = \% Y_2O_3 : \% C_2O_3,$$

$$2Y + 48 : 216 = \% Y_2O_3 : \% C_2O_3.$$

$$Y + 24 : 108 = \% Y_2O_3 : \% C_2O_3.$$

$$Y = \frac{108 \times \% Y_2O_3}{\% C_2O_3} - 24.$$

TABLE I

DATA OF ATOMIC WEIGHT DETERMINATIONS

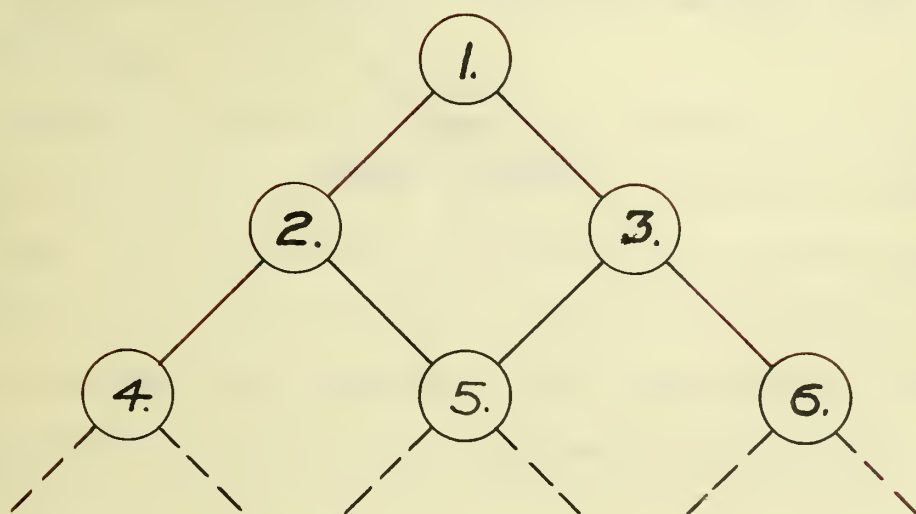
Fraction	Weight (grams)	% C_2O_3	% Y_2O_3	Atomic Weight
1.	10.0	41.39	48.50	103.6
2.	28.3	Not determined		
3.	34.9	41.80	47.84	99.7
4.	31.9	Not determined		
5.	60.0	42.49	46.65	94.6
6.	104.1	42.89	46.00	91.8
7.	44.7	43.36	45.40	89.1
8.	6.6	43.15	45.20	89.1
9.	12.0	43.315	45.30	88.9
10.	5.8	43.98	45.965	88.8

The atomic weight of the original material was 91.85. From the high atomic weight and color of the first fraction, it shows that erbium and holmium are rapidly removed. The fall in the atomic weights of the earlier fractions is slower than that of the later fractions, which is probably due to the varying rate of precipitation. The increase in the percentage of Ce_2O_3 and the decrease in the percentage of Y_2O_3 is exactly what is to be expected as more and more of the holmium and erbium are removed. Owing to the lack of time, it was not considered necessary to determine the atomic weights of fractions two and four. From the results obtained, it was evident that the nitrite method affords a rapid separation of yttrium from erbium and holmium. The ease of manipulation in carrying out the fractionation and the recovery and purification of the fractions are points in its favor. In addition, sodium nitrite is an available reagent and the cost does not make its use prohibitive.

V. THE SEPARATION OF ERBIUM AND HOLMIUM BY FRACTIONAL CRYSTALLIZATION OF THE BROMATES

In addition to the fractional precipitation method for the separation of the rare earths, is the fractional crystallization method which is used to good advantage. When a salt of a mixture of rare earths is subjected to fractional crystallization, the less soluble salts tend to concentrate at the less soluble end of the series and the more soluble salts at the opposite end of the series. The whole material (1) is crystallized and the crystals (2) are separated from the mother liquor (3). The crystals are dissolved and again crystallized, the crystals becoming (4) and the mother liquor (5). The mother liquor (3) is evaporated to crystallization and the crystals are combined with (5) while the mother liquor formed (6) and so on indefinitely. (See page 11 a.)

The fractional crystallization of the bromates was used to separate the erbium and holmium. The crystallization at first was carried out in large flasks, but, as the fractions became smaller, the material was transferred to smaller flasks. The crystals were dissolved on the steam bath in about one half their volume of liquor. A small crystal was allowed to remain in the bottom of the flask so as to form a nucleus for the formation of crystals, as the solution had a tendency to become supersaturated and not crystallize. The surface of the liquor was covered with a thin layer of water to prevent evaporation from the surface of the solution during cooling and thereby securing a better separation. The material after being dissolved was allowed to stand for about a day



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before the process was repeated. This length of time was thought to be sufficient for equilibrium to be established.

The bromates are prepared by using barium bromate, which in turn is formed by mixing boiling solutions containing the required amounts of barium chloride and potassium bromate. As potassium bromate can be prepared cheaply, the rare earth bromates are not costly to obtain. According to James and Bissel¹ the order of solubility of the rare earth bromates is as follows arranged in order of increasing solubility: Eu (least soluble), Gd, Tb, Dy, Ho, Y, Er, Tm, Yb, Lu, Ct, and Sc.

About 25 crystallizations were carried out in the Bb series and about 20 in the Bn series. During the process of separation, several small fractions from the insoluble end of both series were set aside as they contained mostly barium bromate and an earth giving a colorless salt, yttrium. The composition of the fractions was determined by the color and the absorption spectra.

1. J.A.C.S. 36 2060 (1914).

TABLE II, SERIES Bn

Fractions	Color	Absorption Spectra
23	Colorless	Faint Ho band.
24	Very slight pink	Ho, very faint Er band.
25,26	Slight Pink	Ho, faint Er band.
27,28	Pale pink	Fainter Ho band, Er.
29,30	Pink	Faint Ho band, Er.
31,32	Very pink	Er, trace Ho.
33,34	Rosy pink	Er.

TABLE III, SERIES Bb

Fractions	Color	Absorption Spectra
6,7	Colorless	Trace Ho, Yt.
8,9,10,11	Yellowish tinge	Ho, very faint Er band, Yt.
12,13	Very slight pink	Ho, faint Er band, Ho.
14,15	Slight pink	Faint Ho and Er bands Yt.
16,17	Very light pink	Er, Yt, very faint Ho band.
18,19	Light pink	Er, Yt.
20,21	Pink	Intense Er band, small amount Yt.
22	Dark pink	Er.

The most soluble fraction is very pink and gives an intense erbium spectrum. The least soluble portion forms brilliant colorless crystals. The absorption spectrum of this fraction shows faint holmium lines. Even when the erbium lines are still weak,

the salt assumes a pink color which deepens to a rosy pink and intense erbium lines are produced.

VI. SUMMARY

1. The purification of yttrium by fractional precipitation with sodium nitrite proves to be a simple, rapid, and efficient method which is substantiated by the values of the atomic weights of the various fractions.

2. The separation of erbium and holmium is made possible by the fractional crystallization of the bromates, although it is difficult to remove the last traces of erbium from holmium.

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